

PATENT SPECIFICATION

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(54) A METHOD OF SCAVENGING SULPHIDE

- (71) We, HALLIBURTON COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 1015 Bois d'Arc Street, P.O. Drawer 1431, Duncan, Oklahoma 73533, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-
- The present invention is concerned with the scavenging of sulphide from liquids.
- Liquids used in wells penetrating subterranean formations (for example, drilling, completing or servicing liquids used in oil wells or gas wells), liquids produced from and make-up liquids used in such wells, and liquids in sewerage systems frequently contain sulphides, such as hydrogen sulphide.
- Hydrogen sulphide is poisonous and promotes corrosion of steel pipes and tubes which come into contact with liquids containing it. It has therefore been proposed to remove hydrogen sulphide from such liquids either as it is formed or after the liquid has been contaminated by hydrogen sulphide. This process is known as "scavenging".
- It has been proposed in U.S. Patent 3928211 to use zinc hydroxide, zinc carbonate or basic zinc carbonate as the scavenging agent. We have found that these compounds tends to form an insoluble precipitate in which the zinc is unavailable for reaction with hydrogen sulphide, and tend to adversely affect the rheological properties of some liquids, particularly where the liquid contains a clay. Typical adverse effects on the rheological properties include undesired thickening or gelling of the liquid and increased liquid loss.
- We have now developed an improved class of scavenging agents for this purpose. According to the invention, there is provided a method of scavenging sulphide from a liquid having a pH of 5 to 12, in which there is used as the scavenging agent a complex formed between at least one zinc compound and an organic chelating agent, the complex having a stability constant of 10 to 16.
- The scavenging agents used in the method according to the invention have little or no adverse effect on the rheology of the liquid, for example, they do not cause flocculation of clays in the liquid, and the stability constant is such that insoluble zinc hydroxide or zinc oxide is not formed to any appreciable extent.
- The complex has a stability constant of 10 to 16, as mentioned above. The term "stability constant" is defined in "Organic Sequestering Agents" by S. Chaber and A.E. Martell; John Wiley and Sons, Inc., New York, and in "Stability Constants of Metal-Ion Complexes" by L.G. Sillen and A.E. Martell; Metcalf and Cooper Limited, London (1964).
- The scavenging agent used in the method according to the invention may be added to the liquid as a previously prepared complex (either in liquid concentrate, or dry powder form or pre-mixed with water) or, preferably, the complex may be formed *in situ* by reaction of the zinc compound with the chelating agent in the desired ratio in the liquid to be treated. In the latter case, when the liquid to be treated is oil-based (or a dispersion, such as an emulsion, of an oil), it is sometimes desirable to add the zinc compound in the form of a

cracking of metals and liberation of hydrogen sulphide at the surface.

When the complex is formed *in situ*, the organic chelating agent should be combined with the soluble zinc compound in a certain weight ratio depending on its sequestering ability. For NTA and similar chelants the preferred range is about 4:1 to 99:1, more preferably from about 4:1 to 9:1.

In the scavenging agent according to the invention, zinc effectively stops stress cracking of ferrous metals without plating out on the metal and causing galvanic corrosion. Furthermore, zinc does not cause stress cracking through secondary oxygen reactions. Zinc sulphide precipitates out when the liquid contains sulphides. This precipitate does not adversely affect the well fluid rheology and can be readily removed by conventional methods such as centrifuging, filtering or settling in mud pits.

The scavenging agents according to the invention are effective over a wide pH range (from 5 to 12), but they are preferably used in the pH range of about 6 to 11. The scavenging agents can be used alone or in conjunction with conventional well fluid additives, even other sulphide scavenging agents. The scavenging agents of this invention can effectively remove hydrogen sulphide concentrations from only trace amounts like one ppm up to large amounts such as thousands of ppm or more by simply adding the amount of chelate needed to stoichiometrically react with the sulphide.

In a preferred method according to the invention, the complex is added to a drilling fluid which is preferably an aqueous dispersed or nondispersed fluid. The drilling fluid can also be an oil-based or emulsion fluid. The oil can be any normally liquid hydrocarbon such as aliphatic hydrocarbon, an aromatic hydrocarbon or mixtures thereof. The fluid is typically circulated in the well during drilling and other operations so that the concentration of complex should be monitored to maintain a certain concentration, preferably from about several parts per million (ppm) to several percent, depending on the likely amount of hydrogen sulphide present. Normally, a concentration of up to about five pounds per barrel (ppb) of fluid will be sufficient. The fluid should also be monitored to indicate the presence of any hydrogen sulphide or sulphide ions which would indicate that more complex should be added or that the concentration of the complex in the liquid should be increased. As a safeguard where hydrogen sulphide is not likely to be a severe problem, chelate concentrations of about 0.25 to 0.5 ppb (1.258 to 2.516 grams per litre) should be used to scavenge out trace amounts of sulphides that may not be detected by tests on the surface.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only.

EXAMPLES

Thirty three 350 ml. samples of a water-based drilling fluid were formulated using water containing the following additives: 0.9 ppb NaCl, 1.75 ppb CaCO₃, 16 ppb Wyoming bentonite, 28 ppb Southern bentonite, 4 ppb chrome lignosulphonate dispersant and a fluid loss additive. The pH was adjusted to 9.0 with NaOH. Various sulphide scavenging agents were added in the quantities indicated in the following Table 1. (One ppb is one pound per 42-gallon barrel of total fluid and is equal to one gram per 350 millilitres of fluid or about 3 grams per litre of fluid).

When the fluid contained a zinc-containing scavenging agent, the amount of the latter was such that each fluid contained the same molar concentration of zinc metal.

The effect of some additives on stress cracking was evaluated using prestressed steel bearings in some of the drilling fluids at 150°F with rolling; i.e., ageing or hot rolling the sample for the time indicated in the following Table 1.

The majority of the scavenging agents were synthesized by the following steps:

1. Equimolar quantities of the chelating agent and zinc salt were stirred in a minimum amount of water for 30 minutes.

2. The solution was basified (pH 8-9) with KOH.

3. Absolute ethanol was added to precipitate the chelates, which were filtered and dried.

Zinc NTA complexes were prepared by reacting sodium NTA (NTANa₃) with each of the following: ZnCl₂ and ZnSO₄. These complexes were tested both as slurries and as oven-dried solids.

Some of the fluids were treated with H₂S, as shown in Table 1. When hydrogen sulphide treatment was used, the H₂S was generated from 0.1 M sodium sulphide (Na₂S) with sulphuric acid and the H₂S was bubbled into the drilling fluid sample in a Waring blender. For each 100 ml of 0.1 M Na₂S used, 970 ppm of H₂S was generated for reaction in the drilling fluid. Hydrogen sulphide was bubbled through the sample until H₂S emission was detected by lead acetate paper indicating saturation of the mud with H₂S.

The stability of complexes of lead, zinc, and copper vary according to the metal, chelating agent, pH, etc. With the zinc metal ion chelated by nitrilotriacetic acid (NTA), the

TABLE 1 (Continued)

	Sample No.	Treatment or Additive	
5			5
10	24	Base Fluid with 1 ppb sulphides or 2,494 ppm sulphides. Ageing by hot rolling at 150°F for 16 hours. This base mud contains 4.5 ppb VC-10 chrome ligno-sulphonate dispersant.	10
15	25	Same as Sample 24 with 2.08 ppb basic Zn carbonate containing 45% zinc.	15
	26	Same as Sample 24 with 8.66 ppb ZnNTA containing 21% zinc.	
20	27	Base fluid without treatment or additive.	20
25	28	Same as Sample 24 with 8.6 ppb ZnSO ₄ and Na ₃ NTA mixture containing 21% zinc.	25
	29	Standard base fluid (as Sample 24 without sulphides).	
30	30	Same as Sample 29 with 5 ppb of a mixture of 35:65 weight ratio of ZnSO ₄ :Na ₃ NTA.	30
35	31	Same as Sample 30 with the ratio of 40:60	35
	32	Same as Sample 30 with the ratio of 45:55	
40	33	Same as Sample 30 with the ratio of 50:50.	40

Various properties of the above Samples are indicated in the following Tables 2 to 11.

TABLE 3

Rheology after reaction with H₂S

5		Set 1		5
	Sample No.	1	2	
	Apparent Viscosity	18.5	17.5	
10	600 Reading	37	35	10
	300 Reading	22	21	
	Plastic Viscosity (PV)	15	14	
	Yield Point (YP)	7	7	
	Gel Strength (10 sec.)	4	4	
15	Gel Strength (10 min.)	12	25	15
	API Filtrate (ml/30 min.)	8	8	

20 These tests show that the ZnNTA chelate had a high reactive capacity for H₂S with good rheology and fluid loss.

20

TABLE 4

Initial rheology and fluid loss

25		Set 1		25
	Sample No.	8	9	
	Apparent Viscosity	18	16.5	
30	600 Reading	36	33	30
	300 Reading	23	20	
	Plastic Viscosity (PV)	13	13	
	Yield Point (YP)	10	7	
35	Gel Strength (10 sec.)	3	6	35
	Gel Strength (10 min.)	14	38	
	API Filtrate (ml/30 min.)	7.1	6.4	

40

TABLE 5

Rheology and fluid loss after hotrolling 16 hours at 150°F.

45		Set 1		45
	Sample No.	8	9	
	Apparent Viscosity	18.5	19.5	
50	600 Reading	37	39	50
	300 Reading	22	22	
	Plastic Viscosity (PV)	15	17	
	Yield Point (YP)	7	5	
	Gel Strength (10 sec.)	3	3	
55	Gel Strength (10 min.)	9	3	55
	API Filtrate (ml/30 min.)	6.6	7.6	

60 These tests show that drilling fluid with ZnNTA has good rheology and fluid loss after aging or hotrolling.

60

TABLE 9

Set 1 - Rolled 16 hours

5	Sample No.	Description of Bearing	5
	14	Medium dark; rough surface. no cracks	
	15	Dark; smooth surface; cracked	
10	16	Dark; smooth surface; cracked	10

Set 2 - Rolled 5 hours with 2 Bearings

	20	Dark color; one cracked	
15	21	Black; no cracks	15
	22	Black; no cracks	
	23	Dark; no cracks	

Set 2 -- Rolled 22 Hours

20			20
	17	Both black and cracked	
	18	Both black and cracked	
	19	Both dark; no cracks	
	20	Copper coated; cracked	
25	21	Both black; one cracked	25
	22	Both black; one cracked	
	23	Both black; one cracked	

TABLE II

Sample No.	Ratio of Zinc to Chelant											
	Initial 29	Aging	Initial 30	Aging	Initial 31	Aging	Initial 32	Aging	Initial 33	Aging	Initial 33	Aging
Apparent Viscosity	16	12	16	15	20	15	23	16	31	16	31	16
600 RPM	32	24	33	30	40	30	47	32	62	33	62	33
300 RPM	20	14	21	16	25	17	32	19	49	20	49	20
Plastic Viscosity	13	10	12	14	15	13	15	13	13	13	13	13
Yield Point (#/100 ft. ²)	7	4	9	2	10	4	17	6	36	17	36	17
Initial Gel	4	1	2	1	8	1	13	1	22	2	22	2
10 Min. Gel	90	3	109	5	144	10	187	20	239	28	239	28
pH	--	8.9	--	8.5	--	8.5	--	8.6	--	8.6	--	8.6

TABLE 12

Sample	34	35	36	37	38	39	40
NH ₄ HSO ₃ (gm or ppb)	Base Mud	1	2	4	--	--	--
Zn hydrosulfite (gm or ppb)	--	--	--	--	1	2	4
pH (before NaOH)	--	--	6.0	5.6	--	--	--
Caustic (gm or ppb)	--	--	0.25	0.75	--	--	--
pH (after NaOH)	--	--	7.4	7.6	--	--	--
pH (after Na ₂ S)	11.6	10.4	9.6	9.3	11.4	11.1	7.7
H ₂ S (ppm)	960	550	400	250	400	640	100
pH	11.1	After Hot Rolling	9.7	9.1	11.1	10.9	9.2
H ₂ S (ppm)	480	10.3 300	175	25	340	120	trace

EXAMPLE*Sample 41)*

A polymer type aqueous base mud was prepared using the following recipe based on grams (gm) per a 350 milliliter (ml) sample which is proportional to pounds per 42-gallon barrel (ppb):

5	350 ml	- deionized water	5
10	12 gm	- bentonite clay	10
	0.05 gm	- polyvinyl acetate-maleic anhydride copolymer bentonite extender	
15	0.5 gm	- AMOCO Drilaid 425 polyacrylamide polymer	15
	0.25 gm	- NaOH caustic	

The properties of this mud Sample 41 were measured before aerating using air passed through a Garrett gas train dispersion tube and adding ammonium bisulfite (60% in water) dropwise to the mud. The measured and calculated properties are tabulated in Table 13.

After measuring the initial properties the ammonium solution was added dropwise to Sample 41 at 3 drops per 60 seconds with stirring (one drop = 0.027933 gm of NH_4HSO_3) and the oxygen concentration in ppm was recorded. After twenty minutes, addition of the NH_4HSO_3 solution resumed. Recorded values for drops of solution added, oxygen concentration as measured by a YSI oxygen meter in parts per million (ppm) and time in minutes are as follows:

TABLE 14

	Time	Drops	O ₂ ppm	Time	Drops	O ₂ ppm	
35	0	0	7.8	19:00	57	0.07	35
	1:00	3	7.5	20:00	60	0.07	
	2:00	6	7.0	21:00*	--	0.70	
	3:00	9	6.4	22:00*	--	0.80	
	4:00	12	5.8	23:00*	--	2.00	
40	5:00	15	5.0	24:00*	--	1.85	40
	6:00	18	3.7	25:00*	--	1.75	
	7:00	21	0.9	26:00	--	1.60	
	8:00	24	0.45	27:00	63	1.40	
	9:00	27	0.33	28:00	66	0.55	
45	10:00	30	0.25	29:00	69	0.43	45
	11:00	33	0.20	30:00	72	0.37	
	12:00	36	0.15	31:00	75	0.32	
	13:00	39	0.10	32:00	78	0.26	
	14:00	42	0.09	33:00	81	0.23	
50	15:00	45	0.07	34:00	84	0.18	50
	16:00	48	0.07	35:00	87	0.15	
	17:00	51	0.07	36:00	90	0.14	
	18:00	54	0.07				

55 *Aerating sample

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EXAMPLE

(Sample 43)

A third portion of polymer base mud (Sample 43) was tested, aerated and treated with a solution of 20 grams of sodium sulfite anhydrous, Na_2SO_3 , per 100 ml of solution with deionized water. The properties of Sample 43 are in Table 13. The sodium sulfite solution was added at 3 and 5 drops per minutes with stirring as for the previous samples (one drop equals 0.0262415 gm of Na_2SO_3). The time in minutes, drops of solution and oxygen concentration in ppm are tabulated as follows:

10

TABLE 16

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	Time	Drops	O ₂ ppm	Time	Drops	O ₂ ppm	
	0	0	8.30	22:00	90	6.00	
15	1:00	3	8.28	23:00	95	5.70	15
	2:00	6	8.28	24:00	100	5.20	
	3:00	9	8.28	25:00	105	4.85	
	4:00	12	8.20	26:00	110	4.50	
	5:00	15	8.10	27:00	115	4.15	
20	6:00	18	8.18	28:00	120	3.80	20
	7:00	21	8.11	29:00	125	3.50	
	8:00	24	8.10	30:00	130	3.15	
	9:00	27	8.05	31:00	135	2.73	
	10:00	30	8.0	32:00	140	2.34	
25	9:00	35	7.98	33:00	145	1.90	25
	12:00	40	7.9	34:00	150	1.40	
	13:00	45	7.8	35:00	155	1.00	
	14:00	50	7.71	36:00	160	0.65	
	15:00	55	7.51	37:00	165	0.42	
30	16:00	60	7.35	38:00	170	0.31	30
	17:00	65	7.12	39:00	175	0.25	
	18:00	70	6.92	40:00	180	0.21	
	19:00	75	6.80	41:00	185	0.20	
	20:00	80	6.52	42:00	190	0.18	
35	21:00	85	6.30	43:00	195	0.15	35
	44:00	200	0.15	61:00	245	0.45	
	45:00	205	0.13	62:00	250	0.41	
	46:00	210	0.11	63:00	255	0.37	
	47:00	215	0.10	64:00	260	0.34	
40	48:00	220	0.10	65:00	265	0.31	40
	49:00	225	0.10	66:00	270	0.28	
	50:00	230	0.10	67:00	275	0.25	
	51:00*	--	0.75	68:00	280	0.23	
	52:00*	--	1.62	69:00	285	0.20	
45	53:00*	--	2.30	70:00	290	0.19	45
	54:00*	--	2.55	71:00	295	0.16	
	55:00*	--	2.85	72:00	300	0.15	
	56:00	--	0.30	73:00	305	0.14	
	57:00	--	0.70	74:00	310	0.13	
50	58:00	--	0.65	75:00	315	0.11	50
	59:00	235	0.55	76:00	320	0.10	
	60:00	240	0.50				

*Aerating Sample

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From Samples 34-43 it is readily apparent that zinc hydrosulfite effectively removes both oxygen and hydrogen sulfide from drilling fluids without adversely affecting the rheology of the drilling fluid.

14. A method according to any of claims 1 to 13, in which the amount of the complex is controlled such that the concentration of sulphide ions in the liquid is maintained below a predetermined amount.

5 15. A method of scavenging sulphide from a liquid having a pH of 5 to 12, in which there is used as the scavenging agent a complex substantially as herein described in any of Samples 2, 5, 9, 11, 13, 14, 19, 21, 22, 23, 26, 28, 30 to 33, or 41 to 54. 5

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